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Abstract: The 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (4b) was prepared from the parent diketone by successive reaction with PCl5 and Lawesson reagent in pyridine. This new thioketone 4b was transformed into 1-chlorocyclobutanesulfanyl chloride 5 and chloro 1-chlorocyclobutyl disulfide 9 by treatment with PCl5 and SCl2, respectively, in chlorinated solvents (Schemes 1 and 2). These products reacted with S- and P-nucleophiles by substitution of Cl− at the S-atom; e.g., the reaction with 4b yielded the di- and trisulfides 6b and 11, respectively. Surprisingly, only pentasulfide 12 was formed in the reaction of 9 with thiobenzophenone (Scheme 3). In contrast to 5 and 9, the corresponding chloro 1-chlorocyclobutyl trisulfide 13 could not be detected, but reacted immediately with the starting thioketone 4b to give the tetrasulfide 14 (Scheme 4). Oxidation of 4b with 3-chloroperbenzoic acid (mCPBA) yielded the corresponding thione oxides (= sulfine) 15, which underwent 1,3-dipolar cycloadditions with thioketones 3a and 4b (Scheme 5). Furthermore, 4b was shown to be a good dipolarophile in reactions with thiocarbonylium methanides (Scheme 6) and iminium ylides (= azomethine ylides; Scheme 7). In the case of phenyl azide, the reaction with 4b gave the symmetrical trithiolane 25 (Scheme 8).

DOI: https://doi.org/10.1002/hlca.200590203

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Synthesis and Reactions of a New Cyclobutanethione Derivative

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The 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**4b**) was prepared from the parent diketone by successive reaction with PCl_5 and *Lawesson* reagent in pyridine. This new thioketone **4b** was transformed into α-chloro sulfanylchloride **5** and α-chloro disulfanyl-chloride **9** by treatment with PCl_5 and SCl_2, respectively, in chlorinated solvents (*Schemes 1* and *2*). These products reacted with S- and P-nucleophiles by substitution of Cl^- at the sulfanyl group; *e.g.* the reaction with **4b** yielded the di- and trisulfane derivatives **6b** and **11**, respectively. Surprisingly, only pentasulfane **12** was formed in the reaction of **9** with thiobenzophenone (*Scheme 3*). In contrast to **5** and **9**, the corresponding α-chloro trisulfanyl-chloride **13** could not be detected, but reacted immediately with the starting thioketone **4b** to give the tetrasulfane **14** (*Scheme 4*). Oxidation of **4b** with *m*CPBA yielded the corresponding sulfine **15**, which underwent 1,3-dipolar cycloadditions with thioketones **3a** and **4b** (*Scheme 5*). Furthermore, **4b** has been shown to be a good dipolarophile in reactions with thiocarbonyl methanides and azomethine ylides (*Schemes 6* and *7*). In the case of phenyl azide, the reaction with **4b** gave the symmetrical trithiolane **25** (*Scheme 8*).

1. Introduction. – Despite their interesting chemical and physico-chemical properties, thioketones were considered as unstable compounds, which are accessible only with difficulty. Whereas aromatic thioketones show enhanced stability, aliphatic representatives are much less stable and easily undergo enolization and oligomerization [1][2][4]). At present, it is known that their stability increases significantly by the introduction of bulky substituents or other steric stabilizing effects. In addition to adamantanethione (**1**) [3] and the only recently described 'cage thioketone' **2** [4], thioxo derivatives of 2,2,4,4-tetramethylcyclobutane-1,3-dione **3** [5][6] belong to the most useful and relatively easily available cycloaliphatic thioketones. Generally, the synthesis of thioketones is carried out by replacement of the O-atom of a carbonyl group by an S-atom using *Lawesson's* reagent, a mixture of H_2S and HCl, or P_4S_{10} as thionating reagents [7].

Formulae **1**–**4**

In a recent paper, we reported on the reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dione with PCl_5 which leads to 3,3-dichloro-2,2,4,4-tetramethylcyclobutan-1-one (**4a**) [8]. Now we present the preparation of the corresponding thione **4b** and reactions of this new and stable chlorinated thioketone.

2. Results and Discussion. – Heating of **4a** with P_4S_{10} in pyridine for 6 h led to the thioketone **4b** as a red solid, which was stable at room temperature, similar to the thioketones **3a** and **3b**. Typically, the C=S group of **4b** absorbed in the ^{13}C-NMR spectrum ($CDCl_3$) at 273.0 ppm. In analogy to the corresponding reactions of **3a** and **3b** [9], the new thioketone **4b**

[4]) Furthermore, thioketones are known as substances with very unpleasant odor.

reacted with PCl_5 to yield the relatively stable α-chlorosulfanyl chloride **5**, which was used for further reactions without purification. Treatment of **5** in CH_2Cl_2 at room temperature with thioketones **3a** and **4b** led smoothly to the disulfanes **6a** and **6b**, respectively, in high yield (*Scheme 1*). In this reaction, the *S*-atom of the thioketone acts as a soft nucleophile towards the sulfanyl chloride.

Scheme 1

The substitution of chloride in the SCl group was easily achieved by the reaction of **5** with thioacetic acid, which afforded the acetylated disulfane **7** (*cf.* [9][10]). Compounds of this type have been shown to undergo a deacetylation in the presence of morpholine, and a subsequent intramolecular substitution of chloride is believed to yield a reactive dithiirane [11]. Alternatively, the corresponding thiocarbonyl *S*-sulfide can be formed by elimination of chloride. In the case of **7**, the experiment with morpholine led, unexpectedly, to **4b**, which probably was formed from the intermediate *S*-sulfide by elimination of sulfur.

The reaction of **5** with diethyl or triethyl phosphite yielded exclusively **8**, which is the substitution product formed by the nucleophilic attack of the phosphite P-atom in analogy to the *Arbuzov* reaction [12] (*Scheme 1*).

The treatment of **4b** with SCl_2 in CH_2Cl_2 gave the adduct **9**, *i.e.* an α-chlorodisulfanyl chloride (*Scheme 2*). The reaction of the latter with thioacetic acid led to the trisulfane **10** by an extension of the sulfur chain. Similar to the reaction with **5**, **9** also underwent an addition with the parent thioketone **4b** to give the symmetrical trisulfane **11**.

Scheme 2

In order to test the ability of aromatic thioketones to form non-symmetric trisulfanes of type **11**, an experiment with **9** and thiobenzophenone was carried out. When the reagents were used in a 1:1 molar ratio, only benzophenone was isolated after chromatographic workup. Therefore, the reaction was repeated using an excess of **9** (2:1 ratio) in wet THF. Under these conditions, the symmetrical pentasulfane **12** was isolated along with comparable amounts of benzophenone. A likely reaction pathway leading to **12** is outlined in *Scheme 3*. The first step is the formation of the thiocarbonylium ion **A** by a nucleophilic substitution of chloride. In contrast to similar intermediates appearing in reactions with cycloaliphatic thioketones, which lead to the formation of **6** and **11**, **A** is easily hydrolyzed to give benzophenone and the trisulfane derivative **B**. The excess of **9** intercepts **B** immediately forming the pentasulfane **12**.

Scheme 3

The molecular formula of **12** was confirmed by the elemental analysis. As the spectroscopic data were not indicative for the structure, an X-ray crystal-structure determination was performed (*Fig. 1*).

Fig 1. *ORTEP Plot* [13] *of the molecular structure of* **12** (arbitrary numbering of atoms; 50% probability ellipsoids)

In accordance with the results obtained with other polysulfanes [14], the S-chain adopts a helical conformation with torsion angles close to 90º and, as observed in a previously described pentasulfane structure [15], it completes one full helical turn along its length.

However, unlike the similar pentasulfane with terminal cyclobutanone groups [15], there is no disorder in the crystal structure.

With the aim of preparing the corresponding trisulfanyl chloride **13**, **4b** was treated with freshly distilled S_2Cl_2 in CH_2Cl_2 at room temperature. The decoloration of the mixture was significantly slower than in the reaction with SCl_2, and after usual workup, the tetrasulfane **14** was isolated exclusively (*Scheme 4*). Apparently, the slowly formed **13** instantaneously reacts with thioketone **4b** to give the final product in almost quantitative yield.

Scheme 4

The oxidation of thiocarbonyl compounds leads to their *S*-oxides (sulfines), which differ in stability significantly, depending on the substitution pattern [16]. It is well established that sulfines react smoothly with 1,3-dienes and 1,3-dipoles along the activated C=S bond to give the corresponding six- or five-membered heterocyclic *S*-oxides [17]. On the other hand, it has been shown recently that sulfines also behave as 1,3-dipoles in [3+2] cycloadditions with thioketones [18][19]. Treatment of **4b** with *m*CPBA in CH_2Cl_2 gave the expected sulfine **15** as a crystalline material (*Scheme 5).* The reaction of **15** with the parent thioketone **4b** and the oxo-analogue **3a**, respectively, was carried out by heating a mixture of equimolar amounts of the reagents without solvent to 110º. The red color of the thioketones disappeared within *ca*. 30 min, and 1,2,4-oxadithiolanes **16** and **17**, respectively, were obtained after crystallization from MeOH. The molecular structure of **17** has been established by X-ray crystallography (*Fig. 2*). The reaction between **4b** and the known sulfine **18** [20] was performed in an analogous manner leading to **19**, which is an isomer of **17**.

Scheme 5

Fig 2. *ORTEP Plot* [13] *of the molecular structure of* **17** (arbitrary numbering of atoms; 50% probability ellipsoids)

The parent thioketone **4b** was also tested as a dipolarophile in reactions with thiocarbonyl *S*-methanides, which were generated by thermal N_2 extrusion from the corresponding 2,5-dihydro-1,3,4-thiadiazoles **20a** and **20b** (*Scheme 6*). The analysis of the reaction mixture by ^{1}H-NMR spectroscopy showed that the cycloaddition occurred regioselectively leading to the 2,2,4,4-substituted-1,3-dithiolanes **21**. These products revealed the characteristic CH_2 absorption in the ^{13}C-NMR spectrum at 41.9 and 43.3 ppm, respectively. The regioselectivity observed in these reactions fits well with the general rules for [3+2]-cycloadditions of cycloaliphatic *S*-methanides with cycloaliphatic thioketones [21].

Scheme 6

The thermal electrocyclic ring opening of aziridines was widely explored for the synthesis of thiazolidines *via* [3+2]-cycloadditions of the reactive azomethine ylides with C=S dipolarophiles (*cf.* [22-24]). Thermolysis of *cis*-1-methyl-2,3-diphenylaziridine (**22**) in boiling toluene in the presence of **4b** afforded a single product whose structure was again established by X-ray crystallography [25] (*Scheme 7*). In accordance with the expected reaction course, the Ph groups are *trans* oriented, *i.e.*, the intermediate 1,3-dipole **23** has been generated by a conrotatory ring opening of **22**.

Scheme 7

In analogy to a previously reported experiment with **3a** and phenyl azide [26], a mixture of **4b** and phenyl azide was heated to 80°. The reaction was significantly slower than with **3a** and, after evaporation of excess phenyl azide, the residue was analyzed by ^{1}H-NMR spectroscopy. The presence of two sets of singlets located at 1.58/1.51 ppm and 1.49/1.20 ppm revealed the formation of two products in comparable amounts. After chromatographic workup, only the product with the signals at lower field was obtained as a colorless solid, which was identified as the symmetric 1,2,4-trithiolane **25** (*Scheme 8*). The second set of signals can be attributed to the imine **26**, which decomposed during chromatography. In contrast to the reaction with **3a** [26], no 1,4,2-dithiazolidine **27** was formed. Obviously, the proposed intermediate thiocarbonyl *S*-imide **28** undergoes a fast electrocyclic ring closure to give the thiaziridine **29**. Sulfur transfer to **4b** yields the reactive thiocarbonyl *S*-sulfide **30** and imine **26**. Finally, interception of **30** by **4b** leads to the isolated trithiolane **25**. This result shows that the replacement of the C=O group of **3a** by CCl_2 influences remarkably the reactivity of the intermediate thiocarbonyl *S*-imide.

Scheme 8

In summary, the presented results show that the new chlorinated thioketone **4b**, which can easily be prepared, is an attractive model for studies focused on the reactivity of thiocarbonyl groups. Of special interest are the chlorinated α-chlorosulfanyl chlorides **5** and **9**, which are suitable for the preparation of polysulfanes and other sulfur-rich products. The replacement of the C=O group in **3a** by the CCl_2 unit (→ **4b**) does not change significantly the properties of the C=S function, *e.g.* the dipolarophilicity of **4b** has been demonstrated in cycloadditions with thiocarbonyl ylides, sulfines, and azomethine ylides. However, the lack of

the stabilizing transannular effect of the C=O group influences the reactivity of the thiocarbonyl *S*-imide **28** in comparison with the analogous 1,3-dipole generated from **3a** [27].

The Authors thank the analytical sections of our institutes for spectra and elemental analyses. Financial support of the *Polish State Committee for Scientific Research* (Grant No. 3 T09A 046 25), the *Swiss National Science Foundation*, and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *G.M.* and *M.W.* thank Mrs. *M. Celeda* for her superior help in separation and purification of some products described in the paper and Dr. *K. Urbaniak* for the preparation of compound **24**.

Experimental Part

1. *General.* See [28]. M.p.'s were determined in capillary using a *Meltemp 2* apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were registered in $CDCl_3$ with a *Tesla BS 687* instrument (80 and 20 MHz, resp.) or a *Bruker 300* spectrometer (300 and 75 MHz, resp.) using TMS (δ_{TMS} = 0 ppm) as an internal standard. IR spectra (KBr pellets or film) with a *Nexus* spectrophotometer. MS (EI or CI) on a *Finnigan-Mat-90* or *Finnigan-SSQ-700* spectrometer. Elemental analyses were performed in the Analytical Laboratory of the University of Zurich or in the Laboratory of the Polish Academy of Sciences (CBMiM) in Lodz.

2. *Starting Materials*. 2,2,4,4-Tetramethylcyclobutane-1,3-dione was prepared from isobutyryl chloride and Et_3N in CH_2Cl_2 [29]. 2,5-Dihydro-1,3,4-thiadiazoles **20a** and **20b** were synthetized from the corresponding thioketones and CH_2N_2 in pentane at 0–5° following known protocols [30][31]. *cis*-1-Methyl-2,3-diphenylaziridine (**22**) was available from *erythro-N*-methyl-1,2-diphenylethanol by treatment with $SOCl_2$ and subsequent cyclisation by using Et_3N or KOH as a base [32]. Phenyl azide was prepared by diazotation of phenylhydrazine as described in [33]. Thioacetic acid, diethyl and triethyl phosphite, sulfur chloride (SCl_2) and disulfur dichloride (S_2Cl_2; b.p. 134-136°) have been carefully distilled prior to their use. 2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-oxide (**18**) was obtained by oxidation of **3a** with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 following the protocol in [34].

3. *Chlorination of 2,2,4,4-Tetramethylcyclobutane-1,3-dione with PCl_5.* A mixture of 2,2,4,4-tetramethylcyclobutane-1,3-dione (9.8 g, 0.07 mol) and PCl_5 (29.2 g, 0.14 mol) in CCl_4 (50 ml) was heated under reflux for 1.5 h. After cooling to r.t., the soln. was diluted with CH_2Cl_2 (20 ml) and washed with sat. aq. $NaHCO_3$ soln. and H_2O (3x). The org. layer was dried (anhydr. $MgSO_4$), and after filtration, the solvent was evaporated. CC on SiO_2 with hexane containing increasing amounts of $CHCl_3$ gave two colorless products.

1,1,3,3-Tetrachloro-2,2,4,4-tetramethylcyclobutane. Less polar fraction. Yield: 2.68 g (15%). Colorless crystals. M.p. 240–241° ([35]: 234–236°).

3,3-Dichloro-2,2,4,4-tetramethylcyclobutanone (**4a**). More polar fraction. Yield: 8.07 g (59%). Colorless crystals. M.p. 69–71° ([35]: 72–73°).

4. *Thionation of* **4a** *using P_2S_5*. To a vigorously stirred (magnetic stirrer) soln. of **4a** (2.93 g, 0.015 mol) in 15 ml of freshly distilled pyridine, P_2S_5 (3.33 g, 0.015 mol) was added

in small portions. The mixture was heated to 130° (oil bath) for 6 h. After cooling to r.t. the mixture was poured into H_2O and extracted with hexane (3x 5 ml). The org. layer was separated and washed with 2 N HCl, with H_2O (3x) and dried (anhydr. $MgSO_4$). After filtration and evaporation, the red solid residue was purified by CC on SiO_2 using hexane with increasing amounts of CH_2Cl_2 as the eluent. Yield of crude *3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione* (**4b**): 2.79 g (88%). M.p. 140–144°[5]). Crystallization from petroleum ether in dry ice gave red crystals. M.p. 133–135°. IR (KBr): 2990*m*, 1466*m*, 1306*s*, 1145*m* (C=S), 1003*w*, 915v*s*, 827v*s*. ^{1}H-NMR: 1.50 (*s*, 4 Me). ^{13}C-NMR: 26.8 (*q*, 4 Me); 73.1 (*s*, C(2), C(4)); 98.0 (*s*, CCl_2); 273.0 (*s*, C=S). EI-MS: 212 (24), 211 (3), 210 (39), 175 (50), 139 (27), 86 (100, $[Me_2C{=}C{=}S]^{+\cdot}$), 71 (55). Anal. calc. for $C_8H_{12}Cl_2S$ (211.15): C 45.50, H 5.73, S 15.19; found: C 45.65, H 5.84, S 15.38.

5. *Reaction of* **4b** *with* PCl_5. A soln. of **4b** (211 mg, 1 mmol) and PCl_5 (416 mg, 2 mmol) in CCl_4 (5 ml) was heated under reflux. After 45 min, another portion of PCl_5 (832 mg, 4 mmol) was added and heating was continued for 15 min until the red color of the soln. disappeared. The mixture was diluted with CCl_4 (10 ml), washed with sat. aq. Na_2CO_3 soln. and with H_2O (2x). After separation, the org. phase was dried ($MgSO_4$) and filtered, the solvent was evaporated, and the oily residue was used for further reactions without purification: 272.0 mg (96%) of *(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)sulfanyl chloride* (**5**). Colorless, thick oil. IR (neat): 3007*m*, 2981*s*, 2940*s*, 1469v*s*, 1453*s*, 1385v*s*, 1371*s*, 1190*m*, 943*m*, 871v*s*, 835v*s*, 803*s*. ^{1}H-NMR: 1.56 (*s*, 2 Me); 1.58 (*s*, 2 Me). ^{13}C-NMR: 24.3 (*q*, 2 Me); 27.4 (*q*, 2 Me); 60.1 (*s*, C(2), C(4)); 89.6 (*s*, C(1)); 97.9 (*s*, CCl_2).

[5]) During the storage at r.t., a slow decomposition of **4b** was observed, and the ^{1}H-NMR spectrum confirmed the formation of growing amounts of dichloroketone **4a**.

6. *Reaction of* **5** *with Cyclobutanethiones* **3a** *and* **4b**. *General Procedure*. To a magnetically stirred soln. of freshly prepared **5** (136 mg, 0.48 mmol) in CH_2Cl_2 (2 ml), the red soln. of 0.48 mmol of the corresponding thioketone was added dropwise at r.t. After 30 min, the solvent was evaporated and the oily residue was triturated with MeOH to yield crystalline products. Analytically pure samples were obtained by recrystallisation

3-Chloro-3-(1′,3′,3′-trichloro-2′,2′,4′,4′-tetramethylcyclobutan-1′-yl)disulfanyl-2,2,4,4-tetramethylcyclobutanone (**6a**). Yield: 57 mg (30%). Colorless crystals. M.p. 116–118° (MeOH). IR (KBr): 2984*w*, 2936*w*, 1789v*s*, 1445*m* (br.), 1366*w*, 1023*w*, 834*m*. ^{1}H-NMR: 1.38, 1.51, 1.52, 1.64 (4*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 23.0, 23.2 (2*q*, 4 Me); 26.4, 26.6 (2*q*, 4 Me); 60.6 (*s*, 2 Me_2C); 69.7 (*s*, 2 Me_2C); 84.8 (*s*, SCCl); 87.2 (*s*, SCCl); 98.9 (*s*, CCl_2); 217.2 (*s*, C=O). EI-MS: 438 (1), 368 (20), 366 (15), 213 (31), 177 (44), 159 (43), 141 (85), 131 (100), 105 (26), 86 (86). Anal. calc. for $C_{16}H_{24}Cl_4OS_2$ (438.31): C 43.84, H 5.52, S 14.63; found C 43.72, H 5.56, S 14.65.

Bis(*1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfane* (**6b**). Yield 143 mg (60%). Colorless crystals. M.p. 182–184° (MeOH/CH_2Cl_2). IR (KBr): 3012*s*, 2984*s*, 2942*s*, 1466v*s*, 1443v*s*, 1383v*s*, 1370*s*, 1197*s*, 992*s*, 942*s*, 868v*s*, 833v*s*, 796*s*, 554*s*. ^{1}H-NMR: 1.49 (*s*, 4 Me); 1.62 (*s*, 4 Me). ^{13}C-NMR: 26.48, 26.51 (2*q*, 4 Me each); 60.5 (*s*, 4 Me_2C); 87.2 (*s*, 2 SCCl); 98.7 (*s*, 2 CCl_2). CI-MS: 459 (72), 457 (100), 455 (61). Anal. calc. for $C_{16}H_{24}Cl_6S_2$ (493.21): C 38.96, H 4.90, S 13.00; found: C 38.67, H 4.78, S 12.92.

7. *Reaction of* **5** *with Thioacetic Acid*. To a stirred soln. of **5** (282 mg, 1 mmol) in CCl_4 (5 ml), thioacetic acid (83 mg, 1.1 mmol) in 2 ml of CCl_4 was added in small portions at r.t. After complete addition, the stirring was continued for 30 min, the solvent was evaporated and the residual thick oil was crystallized from hexane: 59 mg (38%) of *1-[(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfanyl]ethan-1-one* (**7**). Colorless crystals. M.p. 48–

50° (hexane). IR (KBr): 2980*w*, 2940*w*, 1740v*s* (C=O), 1470*m*, 1110*s*, 943*m*, 870*m*, 833*s*, 595*s*. ^{1}H-NMR: 1.52 (*s*, 2 Me); 1.61 (*s*, 2 Me); 2.49 (*s*, *Me*CO). ^{13}C-NMR: 26.1 (*q*, 2 Me); 27.1 (*q*, 2 Me); 28.7 (*q*, *Me*CO); 60.1 (*s*, 2 Me_2C); 89.4 (*s*, SCCl); 98.3 (*s*, CCl_2); 193.5 (*s*, Me*C*O). CI-MS: 340 (5), 338 (5), 289 (16), 287 (72), 286 (13), 285 (100). Anal. calc. for $C_{10}H_{15}Cl_3OS_3$ (321.71): C 37.33, H 4.69, S 19.93; found: C 37.44, H 4.72, S 19.65.

8. *Treatment of* **7** *with Morpholine*. A soln. of morpholine (652.5 mg, 7.5 mmol) in Et_2O (3 ml) was cooled to –40° (acetone/dry ice). To the stirred soln. was added dropwise a soln. of **7** (482 mg, 1.5 mmol) in Et_2O (3 ml). The mixture was stirred at –40° (acetone, dry ice) for 4 h. While warming to r.t., the orange color changed to red. After addition of Et_2O (15 ml), the mixture was washed with H_2O (2x 30 ml), the org. phase was dried (anhydr. Na_2SO_4), the solvent evaporated, and the residue (180 mg) analyzed by ^{1}H-NMR spectroscopy. There were no signals of the expected product found. Then, the mixture was separated by prep. TLC (SiO_2, CH_2Cl_2/hexane 1:1). Only **4b** (68 mg, 21%) and decomposition products were obtained.

9. *Reaction of* **5** *with Phosphites.* a) *With P(OEt)$_3$* (Method A). To a stirred soln. of **5** (282 mg, 1 mmol) in CH_2Cl_2 (7 ml) at 0° was slowly added $P(OEt)_3$ (166 mg, 1 mmol). The color of the mixture turned to pale red. After additional stirring for 30 min at r.t., the solvent was evaporated to give **8** as a crude oily product (*ca.* 97%). Crystallization from hexane (–78°) afforded analytically pure **8**.

b) *With HP(O)(OEt)$_2$* (Method B). To a stirred soln. of **5** (501 mg, 1.77 mmol) in CH_2Cl_2 (3 ml) was added a soln. of $HP(OEt)_2$ (166 mg, 1 mmol) in CH_2Cl_2 (3 ml). After keeping for 3 d at r.t., the solvent was evaporated and the crude oily product was crystallized from hexane in dry ice to give pure **8**.

O,O-*Diethyl*-S-*(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)monothiophosphate* (**8**). Yield: Method A: 282 mg (73%), method B: 186 mg (31%). Colorless crystals. M.p. 48–50° (hexane, dry ice). IR (KBr): 3004*m*, 2984*m*, 2942*m*, 1473*s*, 1384*m*, 1263v*s*, 1161*s*, 1052v*s*, 1019v*s*, 831*s*, 742v*s*, 564*s*, 547*s*. ^{1}H-NMR: 1.36 (*td*, $J_{H,H}$ = 7.1, $J_{H,P}$ = 0.8, 2 *Me*CH_2); 1.57 (*s*, 2 Me); 1.67 (*s*, 2 Me); 4.12–4.28 (*m*, MeC*H*$_2$). ^{13}C-NMR: 15.9 (*dq*, $J_{C,P}$ = 7.3, Me); 25.0 (*q*, 2 Me); 27.4 (*q*, Me); 60.4 (*d*, $J_{C,P}$ = 5.2, 2 Me_2*C*); 64.3 (*td*, $J_{C,P}$ = 7.1, Me*C*H_2O); 85.4 (*s*, SCCl); 98.9 (*s*, CCl_2). CI-MS: 404 (33), 402 (100), 400 (96), 385 (49), 383 (47). Anal. calc. for $C_{12}H_{22}Cl_3O_3P$ (383.70): C 37.56, H 5.78, S 8.35, Cl 27.71; found: C 37.58, H 5.63, S 8.17, Cl 27.42.

10. *Reaction of* **4b** *with Sulfur Dichloride* (SCl_2). To a stirred soln. of SCl_2 (536 mg, 5.2 mmol) in CH_2Cl_2 (5 ml), a soln. of **4b** (1.0 g, 4.74 mmol) in CH_2Cl_2 (5 ml) was added dropwise, and the stirring was continued for 30 min. The solvent was evaporated and the crude *1-Chloro-2-(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)disulfane* (**9**) was obtained as a thick, pale yellow oil. Yield: 1.41 g (95%). Distillation in a Kugelrohr at 100°/0.5 Torr gave a colorless thick oil. IR (neat): 3005*s*, 2977v*s*, 2940v*s*, 1469v*s*, 1385v*s*, 1371*s*, 1200*s*, 1171*m*, 994*m*, 871v*s*, 834v*s*, 801*s*. ^{1}H-NMR: 1.52 (*s*, 2 Me); 1.53 (*s*, 2 Me). ^{13}C-NMR: 26.4 (*q*, 2 Me); 27.5 (*q*, 2 Me); 59.9 (*s*, 2 Me_2*C*); 89.9 (*s*, SCCl); 98.2 (*s*, CCl_2).

11. *Reaction of* **9** *with Thioacetic Acid*. To a stirred soln. of freshly distilled **9** (314 mg, 1 mmol) in CH_2Cl_2 (5 ml) at r.t., thioacetic acid (84 mg, 1.1 mmol) dissolved in CH_2Cl_2 (2 ml) was added dropwise. After complete addition, stirring was continued for 15 min. at r.t. and the solvent was evaporated. The crude *1-[(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutan-*

1-yl)trisulfanyl]ethane-1-one (**10**) was obtained as a colorless, thick oil, which crystallized slowly. Yield: 243 mg (69%). Colorless crystals. M.p. 72–74°. IR (KBr): 3007*w*, 2983*m*, 2941*w*, 1732v*s* (C=O), 1466*s*, 1383*m*, 1107v*s*, 944v*s*, 867v*s*, 829v*s*, 800*m*, 591v*s*, 564*s*. ^{1}H-NMR: 1.54 (*s*, 2 Me); 1.55 (*s*, 2 Me); 2.47 (s, *Me*CO). ^{13}C-NMR: 26.3 (*q*, 2 Me); 27.0 (*q*, 2 Me); 29.3 (*q*, *Me*CO); 60.0 (*s*, 2 Me_2C); 90.3 (*s*, SCCl); 98.2 (*s*, CCl_2); 192.3 (*s*, Me*C*O). CI-MS: 319 (78), 317 (100), 287 (28), 285 (38), 200 (77), 175 (53). Anal. calc. for $C_{10}H_{15}Cl_3OS_3$ (353.78): C 33.95, H 4.27, S 27.18, Cl 30.06; found: C 34.29, H 4.09, S 26.34, Cl 30.06.

12. *Reaction of* **9** *with* **4b**. To a stirred soln. of **9** (314 mg, 1 mmol) in CH_2Cl_2 (4 ml) at r.t., a soln. of **4b** (211 mg, 1 mmol) in CH_2Cl_2 (2 ml) was added in small portions. After additional stirring for 30 min, the colorless soln. was evaporated to give a solid material. Crystallization from MeOH/CH_2Cl_2 afforded the analytically pure *bis(1,3,3-trichloro-2,2,4,4-tetramythylcyclobutan-1-yl)trisulfane* (**11**). Yield: 296 mg (56%). Colorless crystals. M.p. 238–240°. IR (KBr): 3010*s*, 2978*s*, 2939*s*, 1469v*s*, 1442*m*, 1385*s*, 1370*s*, 1200*m*, 993*m*, 946*m*, 870v*s*, 833v*s*, 559*s*. ^{1}H-NMR: 1.54 (*s*, 4 Me); 1.55 (*s*, 4 Me). ^{13}C-NMR: 26.8 (*q*, 4 Me); 27.1 (*q*, 4 Me); 60.1 (*s*, 4 Me_2C); 90.7 (*s*, 2 SCCl); 98.3 (*s*, 2 CCl_2). CI-MS: 493 (29), 491 (48), 490 (21), 489 (100), 487 (59), 457 (46), 455 (26). Anal. calc. for $C_{16}H_{24}Cl_6S_3$ (525.28): C36.58, H 4.60, S 18.31, Cl 40.50; found: C 36.58, H 4.49, S 18.07, Cl 40.44.

13. *Sulfur Transfer with Thiobenzophenone; Synthesis of Pentasulfane* **12**. To a stirred soln. of blue colored thiobenzophenone (99 mg, 0.5 mmol) in 1 ml of wet THF (2vol% H_2O), a soln. of **9** (314 mg, 1mmol) in abs. THF (1 ml) was added in small portions. The mixture was cooled in a H_2O/ice bath and stirring was continued for 10 min. The colorless soln. was evaporated and the pale yellow, oily residue was crystallized from mixture of MeOH/CH_2Cl_2 to give 94 mg (32%) of *bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)pentasulfane*

(**12**). Colorless crystals. M.p. 157–159°. IR (KBr): 2997v*s*, 2974*s*, 2935*m*, 1466v*s*, 1450*s*, 1383*s*, 1371*s*, 1198*m*, 1170*m*, 991*m*, 944*m*, 870v*s*, 835v*s*, 800*m*, 559*s*. ^{1}H-NMR: 1.54 (*s*, 6 Me); 1.55 (*s*, 2 Me). ^{13}C-NMR: 26.4 (*s*, 2 Me); 26.5 (*s*, 2 Me); 27.0 (*s*, 4 Me); 60.1 (*s*, 4 Me_2C); 89.8 (*s*, SCCl); 90.1 (*s*, SCCl); 98.4 (*s*, 2 CCl_2). CI-MS: 555 (2), 523 (14), 519 (10), 197 (26), 195 (39), 177 (37), 176 (12), 175 (100). Anal. calc. for $C_{16}H_{24}Cl_6S_5$ (589.41): C 32.60, H 4.10, S 27.20, Cl 36.10; found: C 32.50, H 3.90, S 27.04, Cl 35.70.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH_2Cl_2 by slow evaporation of the solvent.

14. *Treatment of* **4b** *with* S_2Cl_2*; Synthesis of Tetrasulfane* **14**. A soln. of freshly distilled S_2Cl_2 (149mg, 1.1 mmol) in CH_2Cl_2 (1 ml) was added at r.t. in small portions to a stirred soln. of **4b** (211 mg, 1 mmol) in CH_2Cl_2 (1 ml). After complete addition, the solvent was evaporated and the crude *Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutan-1-yl)tetrasulfane* (**14**) was obtained as a colorless solid. An analytically pure sample was obtained after crystallization from MeOH/CH_2Cl_2. Yield: 253 mg (91%). Colorless crystals. M.p. 218–220° (MeOH/CH_2Cl_2). IR (KBr): 3010*s*, 2972v*s*, 2937*s*, 1467v*s*, 1442v*s*, 1384*s*, 1372*s*, 1199s, 1169*m*, 993*m*, 831v*s*, 799*s*, 557*s*. ^{1}H-NMR: 1.54 (*s*, 8 Me). ^{13}C-NMR: 26.4 (*q*, 4 Me); 27.0 (*q*, 4 Me); 60.0 (*s*, 4 Me_2C); 90.1 (*s*, 2 SCCl); 98.3 (*s*, 2 CCl_2). CI-MS: 525 (31), 524 (15), 523 (74), 522 (21), 521 (100), 519 (56), 175 (90). Anal. calc. for $C_{16}H_{24}Cl_3S_4$ (557.35): C 34.48, H 4.34, S 23.01, Cl 38.17; found: C 34.04, H 4.07, S 23.13, Cl 37.96.

15. *Oxidation of* **4b** *with* m-*Chloroperbenzoic Acid*. To a stirred soln. of **4b** (1.0 g, 4.7 mmol) in CH_2Cl_2 (15 ml) at 0° (ice-water bath), *m*CPBA acid was added in small portions until the red color of the soln. completely vanished. After 10 min, the soln. was diluted with CH_2Cl_2 (10 ml) and washed with sat. aq. $NaHCO_3$ soln., 2% aq. soln. of NaOH, and finally

with brine. The org. phase was separated and dried ($MgSO_4$). After evaporation of the solvent, the crude product was obtained as a thick colorless oil. Crystallization from hexane in dry ice afforded colorless, crystalline *3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione S-oxide* (**15**)[6]). Yield: 460 mg (43%). Colorless crystals. M.p. 149–152° (hexane). IR (KBr): 2992*s*, 2934*s*, 2868*w*, 1795*m*, 1467*s*, 1450*s*, 1383*m*, 1368*m*, 1299*s*, 1222*m*, 1150*m*, 1072v*s*, 1015*m*, 916v*s*, 825v*s*, 607*m*. ^{1}H-NMR: 1.61 (*s*, 2 Me); 1.76 (*s*, 2 Me). ^{13}C-NMR: 25.1 (*q*, 2 Me); 28.8 (*q*, 2 Me); 57.8, 61.5 (2*s*, 2 Me_2C); 98.5 (*s*, CCl_2); 204.1 (*s*, C=S). CI-MS: 248 (13), 246 (69), 245 (10), 244 (100). Anal. calc. for $C_8H_{12}Cl_2OS$ (227.15): C 42.30, H 5.32, S 14.11; found: C 42.44, H 5.75, S 14.16.

16. *1,3-Dipolar Cycloadditions of Sulfines* **15** *and* **18** *with* **3a** *and* **4b**. *General procedure*. A soln. of 1 mmol of **15** or **18** and 1 mmol of **3a** or **4b** in 0.5 ml of toluene was heated to 110° (oil bath) for 1.5 h. After cooling to r.t., the solvent was evaporated, the residual solid material was triturated with MeOH, and the solid product was filtered and purified by crystallization.

2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecane (**16**). Yield: 236 mg (54%). Colorless crystals. M.p. 162–163° (MeOH/CH_2Cl_2). IR (KBr): 2976*s* (br.), 2938*s* (br.), 1452*s*, 1375*s*, 1056*w*, 946*m*, 881v*s*, 802v*s* (br.), 778*s*, 570*m*. ^{1}H-NMR: 1.33 (*s*, 4 Me); 1.47 (*s*, 2 Me); 1.58 (*s*, 2 Me). ^{13}C-NMR: 21.4 (*q*, 2 Me); 24.5 (*q*, 2 Me); 28.3 (*q*, 2 Me); 28.7 (*q*, 2 Me); 58.2 (*s*, 2 Me_2C); 59.4 (*s*, 2 Me_2C); 81.8 (*s*, SCS); 98.4, 99.0 (2*s*, 2 CCl_2); 112.3 (*s*, OCS). CI-MS: 456 (8), 455 (6), 405 (25), 404 (12), 403 (65), 401 (61), 171 (100). Anal. calc. for $C_{16}H_{24}Cl_4OS_2$ (438.31): C 43.84, H 5.52, S 14.63; found: C 43.64, H 5.48, S 14.79.

[6]) During storage at r.t., **15** decomposed slowly by elimination of S and converted into **4a**.

2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-8-one (**17**). Yield: 242 mg (63%). Colorless crystals. M.p. 100–101° (MeOH/CH_2Cl_2). IR (KBr): 2974v*s*, 2935*s*, 1772v*s* (C=O), 1456*s*, 1376*s*, 1252*m* (br.), 1046*s*, 1012*s*, 888*s*, 800*s*. ^{1}H-NMR: 1.23 (*s*, 2 Me); 1.33 (*s*, 2 Me); 1.37 (*s*, 2 Me); 1.61 (*s*, 2 Me). ^{13}C-NMR: 17.4 (*q*, 2 Me); 24.6 (*q*, 4 Me); 28.7 (*q*, 2 Me); 58.4 (*s*, 2 Me_2C); 66.1 (*s*, 2 Me_2C); 82.5 (*s*, SCS); 99.0 (*s*, CCl_2); 110.2 (*s*, OCS); 218.7 (*s*, C=O). CI-MS: 402 (22), 400 (31), 385 (75), 383 (100). Anal calc. for $C_{16}H_{24}Cl_2O_2S_2$ (383.40): C 50.12, H 6.31, S 16.73; found: C 49.95, H 6.45, S 16.62.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH_2Cl_2 by slow evaporation of the solvent.

8,8-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-2-one (**19**). Yield: 196 mg (51%). Colorless crystals. M.p. 103–105° (MeOH). IR (KBr): 2966*s*, 2927*m*, 1790v*s* (C=O), 1451*s* (br.), 1374*m*, 1027*w*, 943*m*, 894*m*, 810*m* (br.), 771*s*. ^{1}H-NMR: 1.25 (*s*, 2 Me); 1.35 (*s*, 2 Me); 1.44 (*s*, 2 Me); 1.52 (*s*, 2 Me). ^{13}C-NMR: 20.9 (*q*, 2 Me); 21.1 (*q*, 2 Me); 25.2 (*q*, 2 Me); 28.4 (*q*, 2 Me); 59.6 (*s*, 2 Me_2C); 65.5 (*s*, 2 Me_2C); 79.2 (*s*, SCS); 98.5 (*s*, CCl_2); 113.5 (*s*, OCS); 217.9 (*s*, C=O). CI-MS: 402 (4), 401 (3), 400 (5), 189 (100), 175 (20). Anal calc. for $C_{16}H_{24}Cl_2O_2S_2$ (383.40): C 50.12, H 6.31, S 19.73, Cl 18.49; found: C 49.73, H 6.10, S 16.52, Cl 18.44.

17. *Reactions of* **4b** *with Thiocarbonyl* S*-Methanides. General Procedure*. A stirred red soln. of **4b** (211 mg, 1mmol) and 1.1 mmol of the corresponding 2,5-dihydro-1,3,4-thiadiazole **20** in abs. THF (1 ml) was heated to 45° (oil bath). The evolution of N_2 was monitored with a gas burette attached to the reaction flask. After 5 h, the red color disappeared and the evolution of N_2 ceased; the expected volume of N_2 (*ca.* 25 ml) was collected. After cooling to r.t., the solvent was evaporated and the residue was triturated with

MeOH. After 2 h in the refrigerator, the crude product was filtered and purified by crystallization.

3",3"-Dichloro-2",2",4",4"-Tetramethyldispiro[adamantane-2,2'-(1,3)dithiolane-4',1"-cyclobutane (**21a**). Yield: 230 mg (59%). Colorless crystals. M.p. 92–94° (MeOH). IR (KBr): 2997v*s*, 2977v*s*, 2914v*s* (br.), 2854*s*, 1470*s*, 1451*s*, 1382*m*, 1097*w*, 966*w*, 917*m*, 879*m*, 803*s*. ^{1}H-NMR: 1.35 (*s*, 2 Me); 1.49 (*s*, 2 Me); 1.71–1.81 (*m*, 8 H); 2.02–2.17 (*m*, 6 H); 3.31 (*s*, CH_2). ^{13}C-NMR: 23.3 (*q*, 2 Me); 29.1 (*q*, 2 Me); 26.2, 26.5, 42.1 (3*d*, 4 CH); 36.4, 36.6, 37.5 (3*t*, 5 CH_2); 41.8 (*t*, CH_2S); 55.0 (*s*, 2 Me_2C); 73.4, 74.5 (*s*, 2 C_q); 100.8 (*s*, CCl_2). CI-MS: 395 (17), 393 (71), 391 (100). Anal. calc. for $C_{19}H_{28}Cl_2S_2$ (391.47): C 58.30, H 7.21, S 16.38, Cl 18.11; found: C 58.19, H 7.21, S 16.53, Cl 18.36.

2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-5,10-dithiadispiro[3.1.3.2]undecan-8-one (**21b**). Yield: 148 mg (39%). Colorless crystals. M.p. 143–145° (hexane). IR (KBr): 2971v*s*, 2928*m*, 1773v*s* (C=O), 1453*s* (br.), 1381*m*, 1248*w*, 1170*w*, 1024*s* (br.), 906*m*, 885*m*, 806*s* (br.). ^{1}H-NMR: 1.29 (*s*, 2 Me); 1.53 (*s*, 2 Me); 3.16 (*s*, CH_2). ^{13}C-NMR: 21.9, 23.5, 25.0, 28.9 (4*q*, 4 Me); 43.3 (*t*, CH_2); 56.2 (*s*, 2 Me_2C); 66.2 (*s*, 2 Me_2C); 73.1 (*s*, SCS); 74.3 (*s*, C_q); 100.5 (*s*, CCl_2); 219.9 (*s*, C=O). CI-MS: 385 (18), 383 (75), 381 (100). Anal. calc. for $C_{17}H_{26}Cl_2OS_2$ (381.43): C 53.53, H 6.87, S 16.81, Cl 18.59; found: C 53.59, H 6.98, S 16.58, Cl 18.37.

18. *Reaction of* **4b** *with* cis-*1-Methyl-2,3-diphenylaziridine* (**22**). A soln. of **22** (209 mg, 1 mmol) in abs. toluene (2 ml) was heated under reflux for 30 min. Then, **4b** (211 mg, 1 mmol) was added in small portions, and the mixture was heated under reflux for 6 h. The solvent was evaporated and the solid residue was purified by crystallisation: 200 mg (50%) of trans-*2,2-dichloro-1,1,3,3,7-pentamethyl-6,8-diphenyl-5-thia-7-azaspiro[3.4]octane* (**24**). Colorless crystals. M.p. 194–196° (MeOH/CH_2Cl_2). IR (KBr): 3025*m*, 2977*m*, 2946*s*, 2844*m*,

2797*m*, 1490*m*, 1454*s* (br.), 1381*s*, 1240*m*, 1024*m*, 1142*m*, 1074*m* (br.), 906*s*, 873*s*, 806v*s*, 758*s*, 727*s*, 711*s*, 695*s*. ^{1}H-NMR: 0.87, 1.28, 1.55, 1.69 (4*s*, 4 Me); 1.83 (*s*, MeN); 4.63 (br.*s*, 2 CH); 7.10–7.60 (*m*, 8 arom. H); 8.20–8.50 (2 arom. H). ^{13}C-NMR: 25.5, 27.0, 27.4, 28.7 (4*q*, 4 Me); 35.5 (*q*, MeN); 54.9, 58.3, 71.0 (3*s*, 3 C_q); 71.1, 76.3 (2*d*, 2 CH); 102.1 (*s*, CCl_2); 128.2, 128.4, 128.5, 128.6, 128.8, 132.3 (6*d*, 10 arom. CH); 135.5, 139.8 (2*s*, 2 arom C). CI-MS: 424 (15), 422 (69), 420 (100), 386 (12). Anal. calc. for $C_{23}H_{27}Cl_2NS$ (420.45): C 65.71, H 6.47, N 3.33, S 7.63, Cl 16.86 ; found: C 65.65, H 6.67, N 3.30, S 7.44, Cl 16.36.

19. *Reaction of* **4b** *with* PhN_3*; Synthesis of 1,3,4-Trithiolane* **25**. A stirred soln. of **4b** (422 mg, 2 mmol) in 0.5 ml of freshly distilled PhN_3 was heated to 80° (oil bath). The evolution of N_2 was monitored with a gas burette connected to the reaction flask. After 10 h, the N_2 evolution ceased, and the volume of N_2 was determined to *ca*. 17 ml (1/3 of the stochiometric amount). The excess of PhN_3 was removed in *vacuo* using a Kugelrohr (50°/0.1 Torr). The residual oil was analysed by ^{1}H-NMR spectroscopy, which revealed the presence of two sets of singlet signals located at 1.20/1.49 ppm and 1.51/1.57 ppm, respectively. The first two signals were attributed to the *N*-phenylimine **26**, which decomposed during chromatographic workup on SiO_2. Trithiolane **25** was isolated by prep. TLC using plates precoated with SiO_2 and hexane as the eluent. An analytically pure sample was obtained by recrystallisation. *2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-5,10,11-trithiadispiro-[3.1.3.2]undecane* (**25**). Yield: 110 mg (36%). Colorless crystals. M.p. 183–184° ($MeOH/CH_2Cl_2$). IR (KBr): 2994*s*, 2979*s*, 2937*m*, 1470*s*, 1452*m*, 1442*m*, 1382*s*, 1368*m*, 947*m*, 871*s*, 800v*s*, 566*m*. ^{1}H-NMR: 1.51 (*s*, 4 Me); 1.58 (*s*, 4 Me). ^{13}C-NMR: 25.4 (*q*, 4 Me); 29.4 (*q*, 4 Me); 59.1 (*s*, 4 Me_2C); 88.0 (*s*, 2 SCS); 100.0 (*s*, 2 CCl_2). CI-MS: 456 (59), 454 (100), 419 (82). Anal. calc. for $C_{16}H_{24}Cl_4S_3$ (454.38): C 42.30, H 5.32, S 21.17; found: C 42.64, H 5.23, S 19.48.

20. *X-Ray Crystal-Structure Determination of* **12** *and* **17** (*Table* and *Figs. 1-2*)[7]). All measurements were performed on a *Nonius KappaCCD* diffractometer [36] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1-3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [37]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [38] was applied. Equivalent reflections, other than the *Friedel* pair for **12**, were merged. The structures were solved by direct methods using SIR92 [39], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were not applied. In **12** and **17**, three and one reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [40] of **12** yielded a value of –0.03(5), which confidently confirms that the refined coordinates correspond with the true absolute structure. Neutral atom scattering factors for non-H-atoms were taken from [41a], and the scattering factors for H-atoms were taken from [42]. Anomalous dispersion effects

[7]) CCDC-271077–271078 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

were included in F_c [43]; the values for f' and f'' were those of [41b]. The values of the mass attenuation coefficients are those of [41c]. All calculations were performed using the *SHELXL97* [44] program.

Table. *Crystallographic Data for Compounds* **12** *and* **17**

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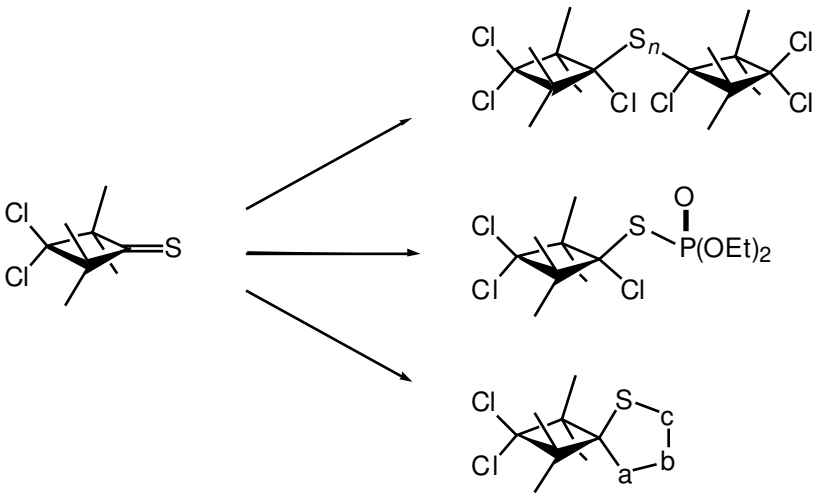
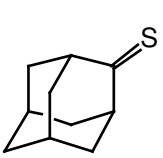
Table. *Crystallographic Data for Compounds* **12** *and* **17**

	12	**17**
Crystallized from	$MeOH/CH_2Cl_2$	$MeOH/CH_2Cl_2$
Empirical formula	$C_{16}H_{24}Cl_6S_5$	$C_{16}H_{24}Cl_2O_2S_2$
Formula weight	589.38	383.39
Crystal color, habit	colorless, prism	colorless, tablet
Crystal dimensions [mm]	0.13 × 0.15 × 0.20	0.10 × 0.23 × 0.25
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	orthorhombic
Space group	*Pc*	*Pbca*
Z	2	8
Reflections for cell determination	20425	56713
2θ range for cell determination [°]	4–55	4-60
Unit cell parameters *a* [Å]	12.9819(2)	11.0298(1)
b [Å]	6.9384(1)	13.3380(2)
c [Å]	14.7339(3)	25.1125(4)
β [°]	112.8723(9)	90
V [Å^3]	1222.79(4)	3694.44(9)
D_X [g cm^{-3}]	1.601	1.378
μ(MoK_α) [mm^{-1}]	1.132	0.581
Scan type	ϕ and ω	ϕ and ω
2θ(max) [°]	55	60
Transmission factors [min; max]	0.721; 0.883	0.750; 0.947
Total reflections measured	27585	64184
Symmetry independent reflections	5533	5407
Reflections with $I>2\sigma(I)$	5023	4040
Reflections used in refinement	5530	5406
Parameters refined; restraints	252; 2	207; 0
Final *R(F)* [$I>2\sigma(I)$ reflections]	0.0314	0.0425
wR(F^2) (all data)	0.0735	0.1164
Weighting parameters [*a*; *b*][a])	0.0406; 0	0.0583; 2.0602
Goodness of fit	1.053	1.036
Final Δ_{max}/σ	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.53; -0.55	0.79; -0.45

a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$

Graphical Abstract





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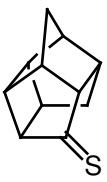

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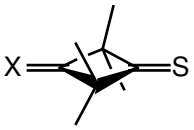

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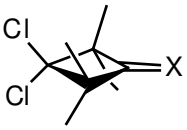
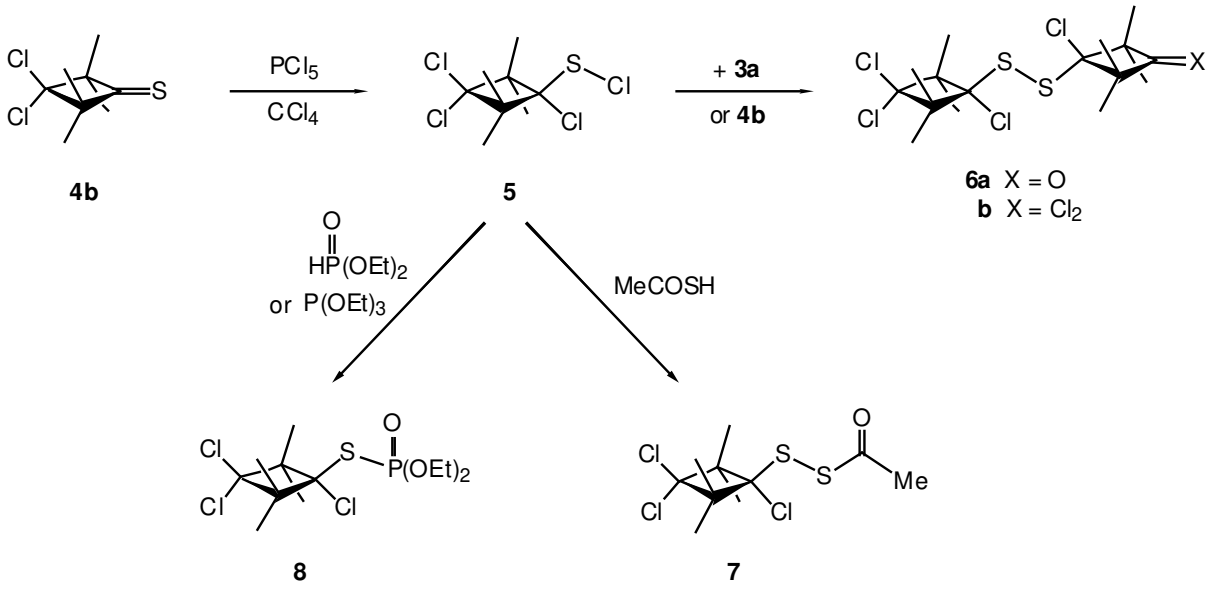
b X = S

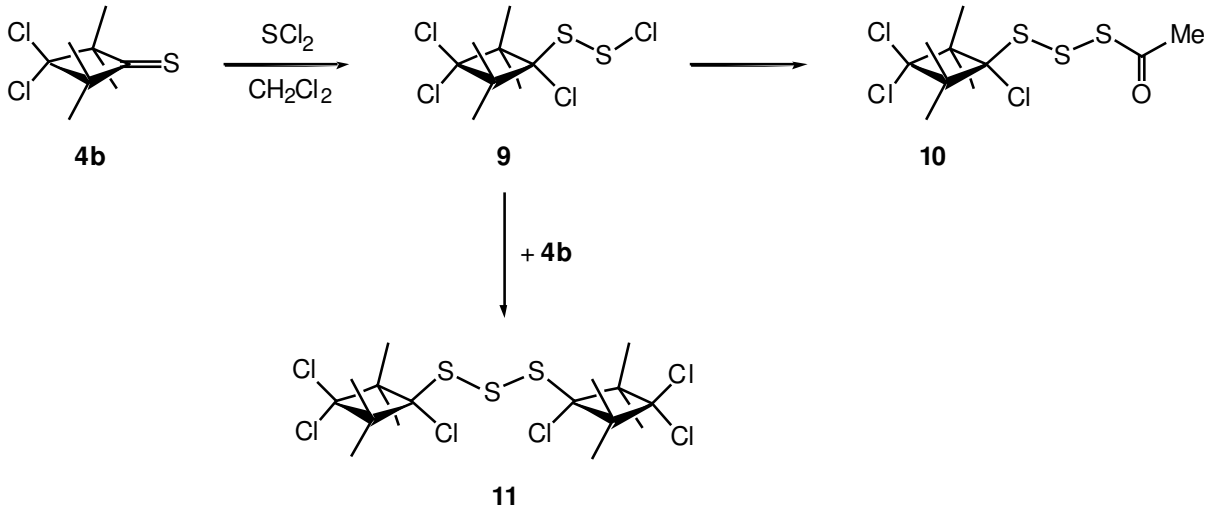


4a X = O
b X = S

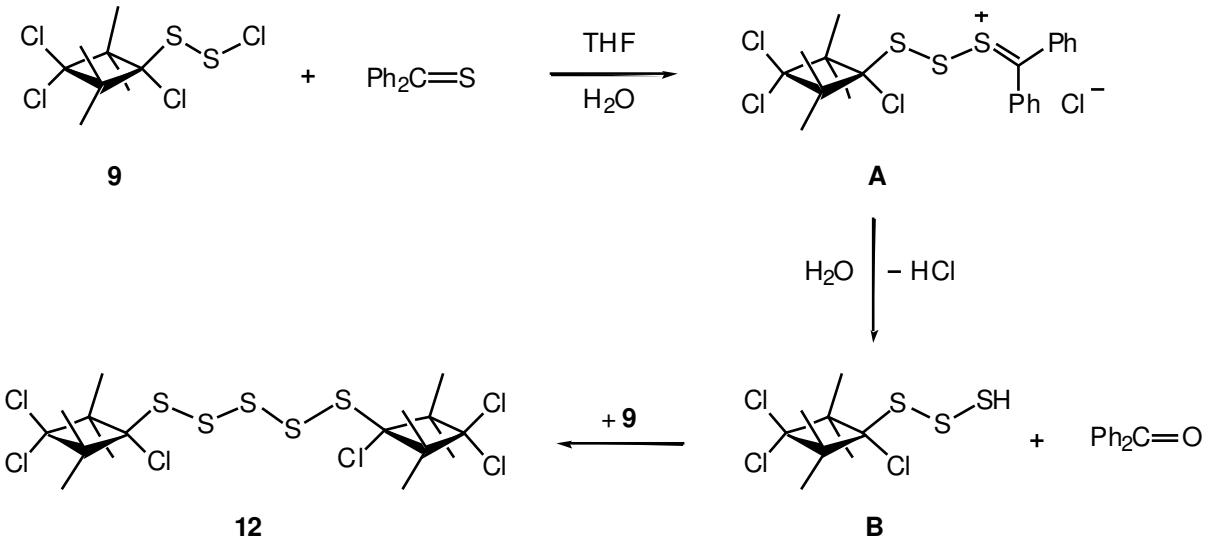
Scheme 1



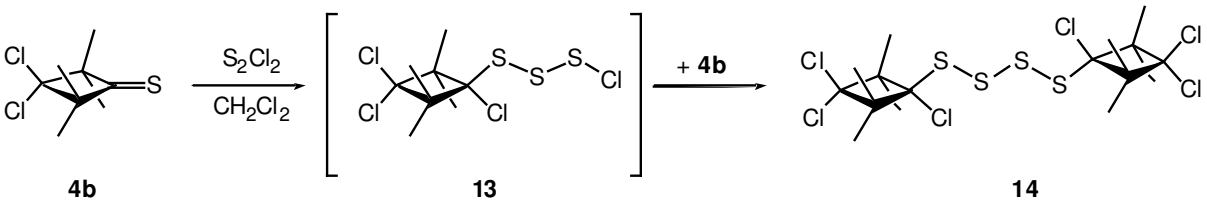
Scheme 2



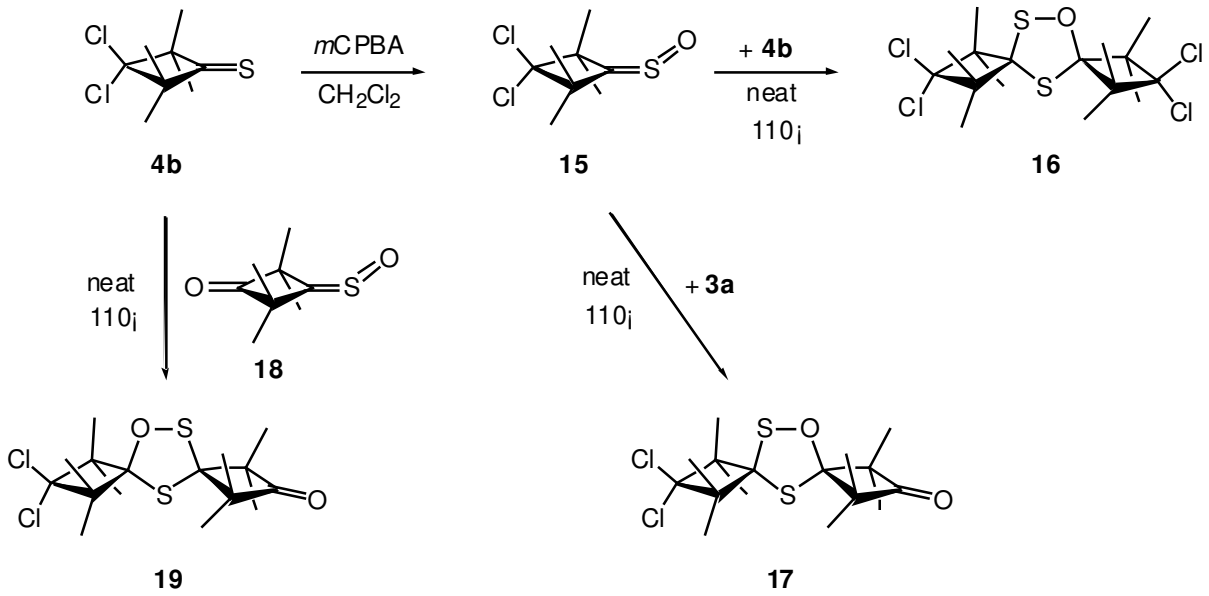
Scheme 3



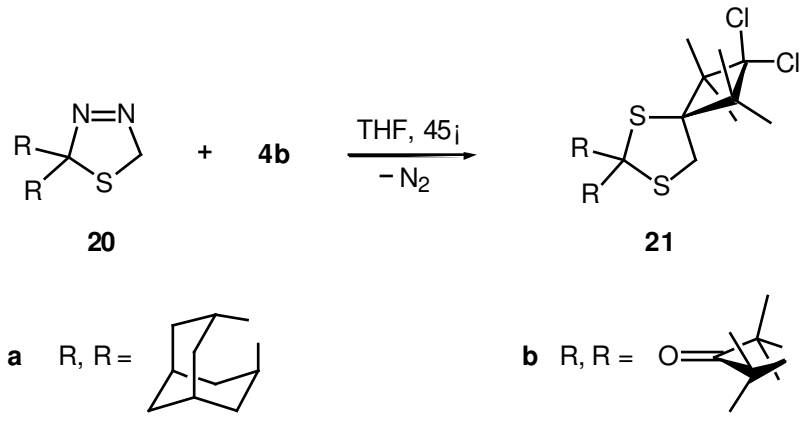
Scheme 4



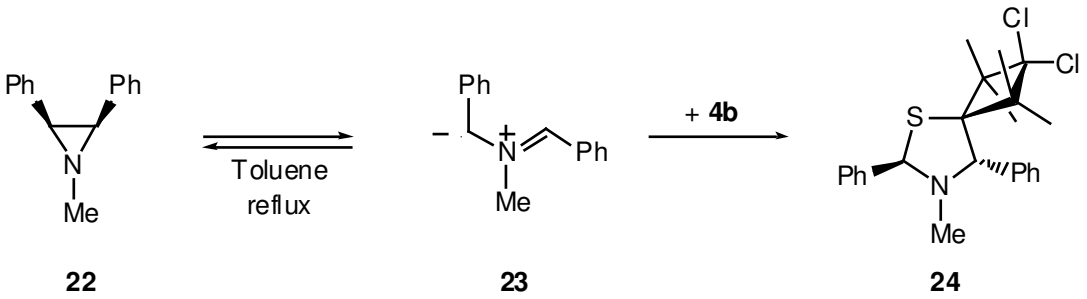
Scheme 5



Scheme 6



Scheme 7



22 **23** **24**

Scheme 8

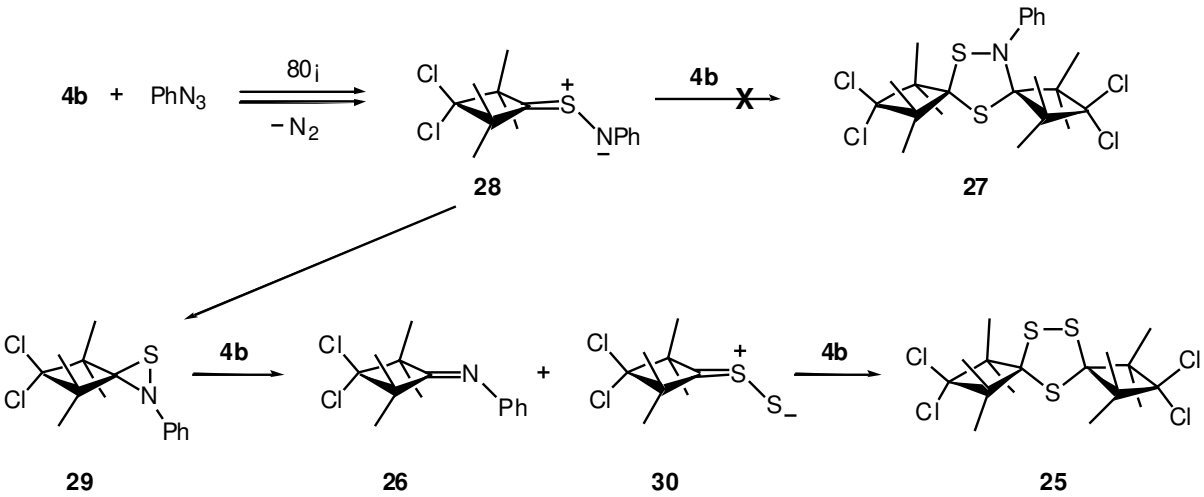


Figure 1

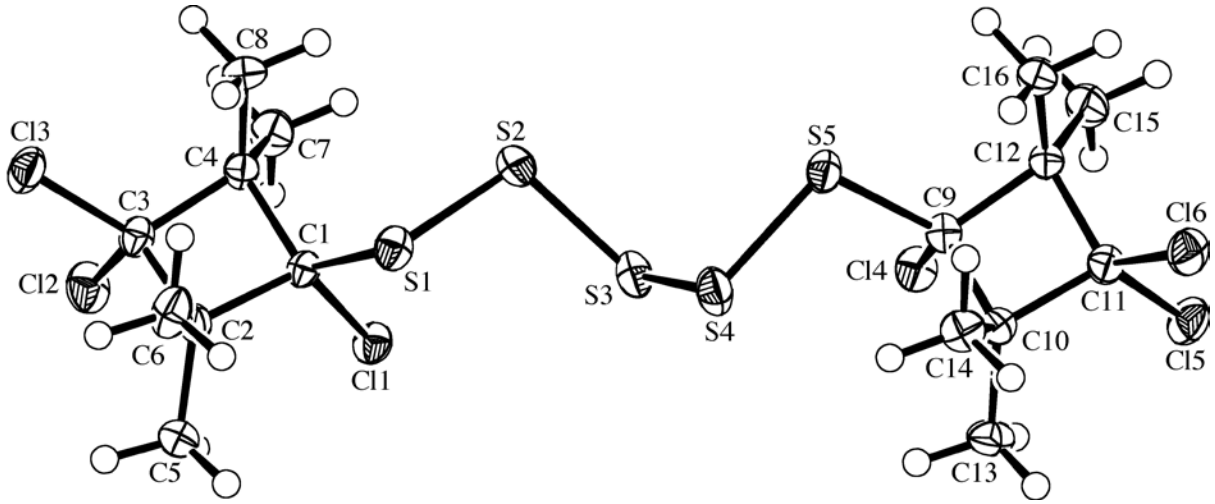


Figure 2